

Electrochemical behavior of 3,6-dihydroxyphenanthrene on boron-doped diamonds

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Abstract

The electrochemical behaviors of 3,6-dihydroxyphenanthrene in non-aqueous or aqueous solutions were investigated using boron-doped diamond electrodes. 3,6-Dihydroxyphenanthrene exhibited different cyclic voltammetric behaviors in organic and aqueous solutions. Cyclic voltammetry, hydrodynamic voltammetry and flow injection analysis (FIA) with amperometric detection were used to study the oxidation reactions. Experiments were concurrently performed using glassy carbon electrodes as comparison. The detection limit of 5 μM for 3,6-dihydroxyphenanthrene in organic medium was obtained by the use of the FIA technique with the diamond electrode. The peak current at +1.2 V vs. Ag/AgCl due to the oxidation of 3,6-dihydroxyphenanthrene is proportional to its bulk concentration in the range of 10–100 μM with $R=0.99$. The FIA response was highly reproducible, and the response variation was below 6% from film to film in detectable range.

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1. Introduction

Although the practical application is still in its infancy, heavily boron-doped diamond (BDD) is indeed superior as an electroanalytical electrode due to wide electrochemical potential windows in both non-aqueous and aqueous solution [1–3], very low voltammetric background current [4], high resistance to deactivation via fouling, extreme electrochemical stability, and high sensitivity. The further investigations showed that lack of oxygen functional groups and highly hydrophobic on inert surface of diamond fabricated via chemical vapor deposition (CVD) [5] are mainly responsible for the superior performance of diamond electrodes.

To the best of our knowledge, this is the first report on the electrochemical investigations of 3,6-dihydroxyphenanthrene. The results show that BDD electrodes are superior to glassy carbon (GC) electrode as electrochemical sensor in both non-aqueous and aqueous solutions due to high sensitivity, stability and reproducibility. BDD is demonstrated to be an excellent electrode material for the detection of 3,6-dihydroxyphenanthrene especially

in organic solution due to high sensitivity, even at high oxidation potentials.

2. Experimental

Heavily BDD film was deposited on p-Si(111) wafer. Microwave plasma (2.45 GHz) assisted CVD system (ASTeX Ax2115) was used to grow diamond film. High-quality microcrystalline diamond thin film was deposited at a forward power of 1400 W, a system pressure of approximately 70 Torr, a chamber temperature of 540 °C. Ultra purity hydrogen gas and the mixture of acetone and methanol were used as respective carrier gas and carbon source in our laboratory. Film with an average thickness of 20 μm was obtained after 24-h deposition. The GC electrodes were prepared by polishing on polishing cloth in alumina/water slurries. Both diamond and GC were ultrasonicated in deionized water. Ohmic contacts for diamond and GC electrodes were made by gold paste (Tokuriki Chemical Co.). The electrodes were mounted using liquid silicone resin covering the periphery of BDD or GC films with exposed area of 0.20 cm^2 .

Electrochemical measurements were carried out in a single compartment cell with Ag/AgCl as the reference electrode and platinum mesh as the counter electrode.

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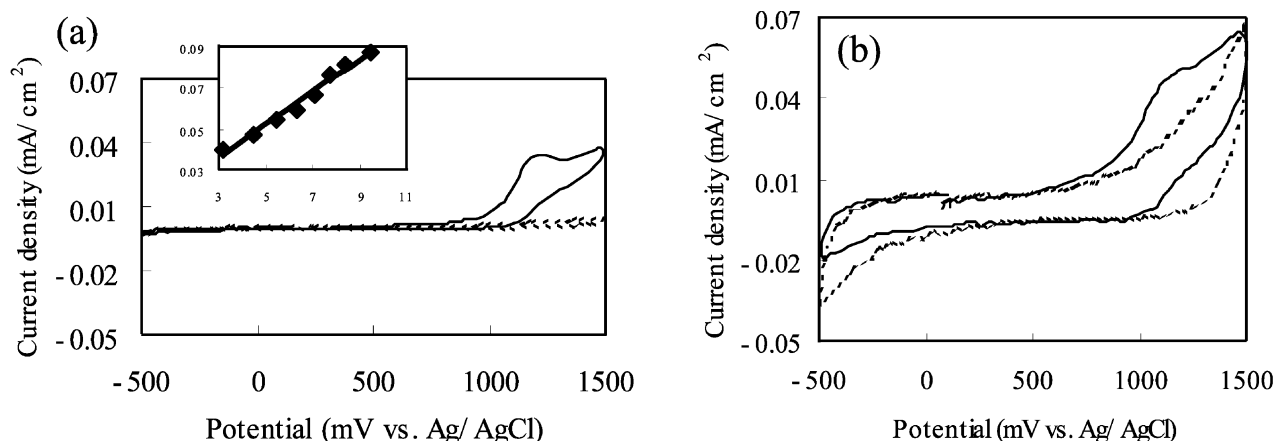


Fig. 1. Cyclic voltammograms for 100 μM 3,6-dihydroxyphenanthrene in MeCN/0.01 M Bu_4NPF_6 at (a) BDD, (b) GC, sweep rates were 30 mV/s, solid lines are signal curves and dotted lines are background ones. Inset of (a) is correlative curve of i_{p2} and $v^{1/2}$.

Cyclic voltammograms were recorded with a combined potentiostat-function generator controlled by a PC.

The flow injection analysis (FIA) system was used in the present study. The mobile phase flow was regulated with a model pump (EYELA SMP-23), through a model injector valve with a 20- μl injection loop, and into a home-built thin-layer flow cell. The flow rate was 1.0 ml/min. 0.01 M $\text{Bu}_4\text{NPF}_6/\text{MeCN}$ was used as the mobile phase. The sample solutions were prepared with the same media.

Hydrodynamic voltammogram was obtained before FIA. The data were obtained by recording the background current at a fixed potential, followed by the injection of the 20-analyte samples. The peak current after each injection was recorded, together with the corresponding background current.

3,6-Dihydroxyphenanthrene was synthesized [6]. Other analytical grade reagents were used as purchased without further purification.

3. Results and discussion

3.1. Voltammetric studies

Fig. 1 shows cyclic voltammograms obtained for 3,6-dihydroxyphenanthrene in deaerated 0.01 M $n\text{-Bu}_4\text{NPF}_6/\text{MeCN}$ media at BDD and GC electrodes. In the case of BDD the voltammogram exhibit a shoulder peak at $E_{p1}=1.00$ V and a well-defined peak at $E_{p2}\approx 1.20$ V, whereas that for GC tends to a plateau ($E_{1/2}\approx 1.00$ V). No reduction peak was observed on the reverse scan. Also, the peak current i_{p2} in the present system was linearly dependent on sweep rate $v^{1/2}$ with a slight deviation from the origin, indicating a semi-infinite linear diffusion of reactant to the electrode. It is worth noting that the very low background current was observed on BDD electrode, which is in contrast to that on GC electrode, the background was 1 order of magnitude less for the former electrode than that for the

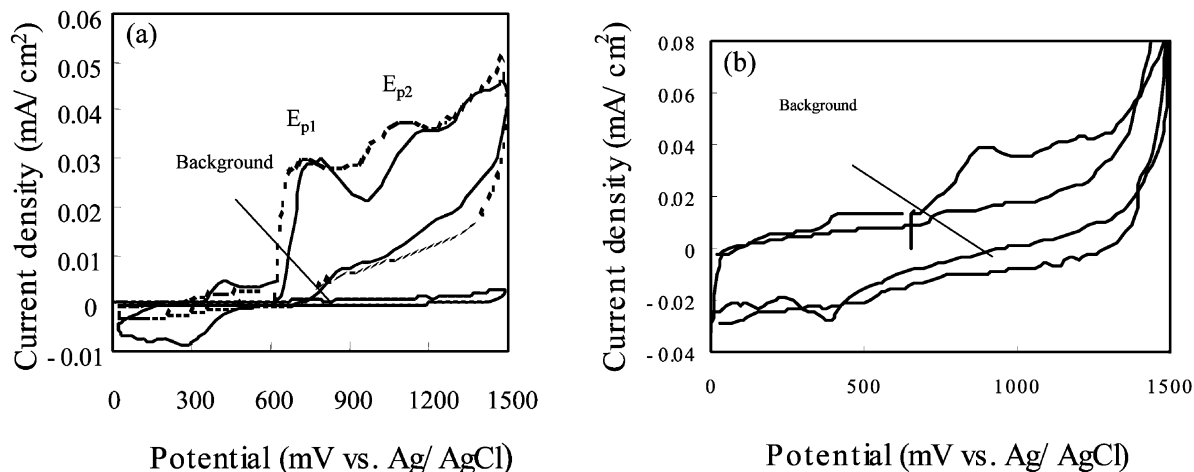
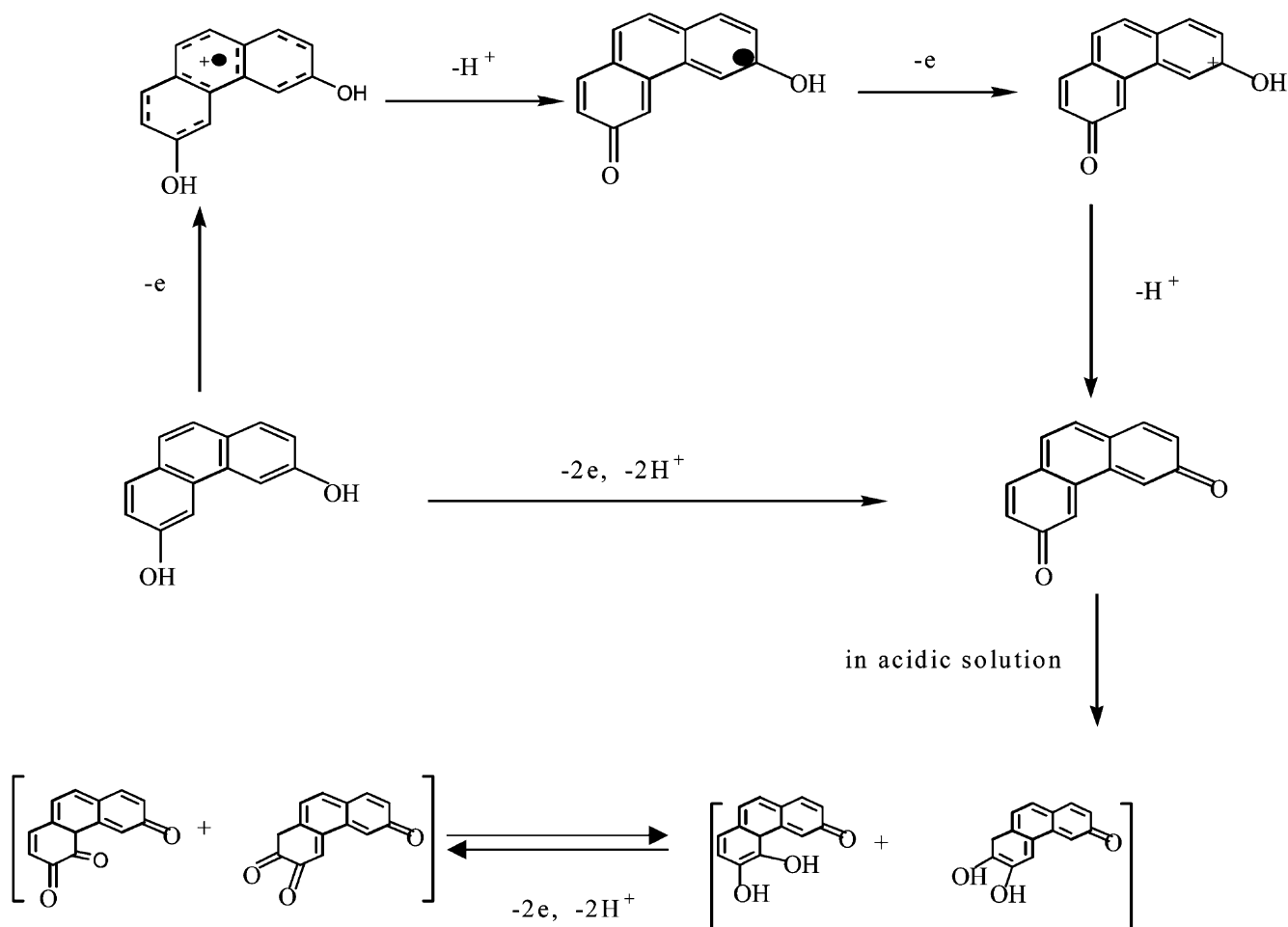


Fig. 2. Cyclic voltammograms for 100 μM 3,6-dihydroxyphenanthrene in 1 M $\text{HClO}_4 + 0.01$ M NaClO_4 (solid) and 1 M $\text{NaClO}_4 + 0.01$ M HClO_4 (dotted) at (a) BDD and (b) GC, sweep rates: 30 mV/s.

Reaction Scheme



Scheme 1. Reaction scheme.

latter electrode. To 100 μM 3,6-dihydroxyphenanthrene, the S/N ratios (for i_{p2}) were 1 order of magnitude higher for the diamond electrode (9) than that for the GC electrode (1). The low background current and the high S/N ratio associated with the diamond electrode make high sensitivity for 3,6-dihydroxyphenanthrene detection in $n\text{-Bu}_4\text{NPF}_6/\text{MeCN}$ media, even though the peak potential is relatively positive.

Fig. 2 shows the voltammograms performed in 1 M $\text{HClO}_4 + 0.01$ M NaClO_4 and 1 M $\text{NaClO}_4 + 0.01$ M HClO_4 aqueous solutions. Two anodic peaks (E_{p1} and E_{p2} in Fig. 2a) located at the potential of 0.78 and 1.2 V, respectively, appeared when the potential was swept positively from the rest potential in 1 M $\text{HClO}_4 + 0.01$ M NaClO_4 system. The potentials of both peaks E_{p1} and E_{p2} shifted positively approximately 100 mV in 1 M $\text{NaClO}_4 + 0.01$ M HClO_4 system, indicating that both anodic reactions being pH-dependent. On the consecutive potential sweeping, a couple of redox peaks observed in the former solution system with the ΔE_p value being 122 mV centered at 0.34 V, whereas a

couple of ill-defined redox peaks centered at 0.29 V observed in the latter case. At GC, the couple of redox peaks is centered at 0.45 V with the ΔE_p of 30 mV,

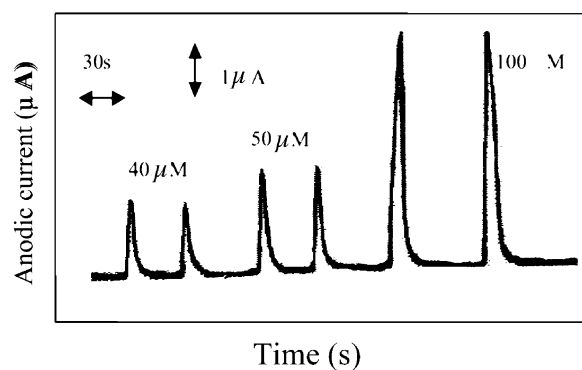


Fig. 3. Electrochemical detection results for FIA with 20- μl injections of 3,6-dihydroxyphenanthrene in $\text{MeCN}/0.01$ M Bu_4NPF_6 . The applied potential was 1.3 V vs. Ag/AgCl and the flow rate was 1 ml/min.

which is characteristic of two-electron transfer electrode reaction.

Based on the investigations above, we can give the electrode reaction mechanism of 3,6-dihydroxyphenanthrene in both organic and aqueous media. The reaction scheme is shown as follows in Scheme 1. The electrochemical oxidation of 3,6-dihydroxyphenanthrene is believed to take place at the two phenol groups of the molecules to form the corresponding 3,6-dihydroxyphenanthredione in both organic and aqueous solutions. The hydroxy groups of *o*-directors and the ketone groups of *o*-directors on phenanthrene is reversibility redox couples verified by the cyclic voltammetric behavior of 9,10-phenanthrenequinone in 1 M HClO₄ + 0.01 M NaClO₄ aqueous solution (not shown here), consequently, it is shown that the reversibility redox peaks appeared approximately at 0.34 and 0.45 V at BDD and GC electrodes in the same solution are due to the hydroxy groups of *o*-directors formation in aqueous solution. In acidic solution, via coupled chemical reaction, ketone group is further reduced to the corresponding phenols, which further reversibly react on electrode.

3.2. Flow injection analysis

A sigmoidally shaped hydrodynamic voltammogram *i*–*E* curves were obtained for 20- μ l injections of 100 μ M 3,6-dihydroxyphenanthrene in 0.01 M Bu₄NPF₆/MeCN. At the potentials beyond 1300 mV, the current

curve is characteristic of limiting current, so we adopted 1300 mV as detection potential for FIA.

Fig. 3 shows the amperometric response of a BDD electrode for repetitive 20- μ l injections of 3,6-dihydroxyphenanthrene in 0.01 M Bu₄NPF₆/MeCN using detection potential of 1300 mV. The signal current increased linearly with increasing the concentration of 3,6-dihydroxyphenanthrene from 10 to 100 μ M ($R=0.99$). The response variation was maximum approximately 6% from film to film. Well-defined and reproducible amperometric responses were also observed for 10- μ M injection samples. The detection limiting for 3,6-dihydroxyphenanthrene in 0.01 M MeCN/Bu₄NPF₆ was 5 μ M. BDD electrodes showed complete stability for at least 24-h exposure to laboratory atmosphere. The results verified the outstanding performance of BDD electroanalysis for 3,6-dihydroxyphenanthrene in organic solution using FIA technique.

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